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(54) PREPARATION OF N-PHOSPHONOMETHYL GLYCINE
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(56) 56277/73 480023 C07F 9/38
(57) Claim

1. Process for the preparation of N-phosphonomethyl-glycine by oxydating N-phosphonomethyl imino diacetic acid with oxygen or a gas containing oxygen under heating or stirring in (conventional) at a temperature of between room temperature and 200°C the presence of a catalyst which comprises oxydating N-phosphonomethyl imino diacetic acid in an aqueous suspension therefore.

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Form 10

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Complete Specification for the invention entitled:

PROCESS FOR THE PREPARATION OF N-PHOSPHONOMETHYL GLYCINE

The following statement is a full description of this invention, including the best method of performing it known to us

PROCESS FOR THE PREPARATION OF N-PHOSPHONOMETHYL GLYCINE

The present invention relates to an improvement in the process for the preparation of N-phosphonomethyl glycine by oxydation of N-phosphonomethyl imino diacetic acid with oxygen or a gas containing oxygen in the presence of a catalyst.

N-phosphonomethyl glycine has been known and widely used for almost a decade for its herbicidal activity. N-phosphonomethyl glycine (Glyphosate) is suitable for the control of various monocotyledonous and dicotyledonous annual and perennial/undesired plants in case of post-emergent treatment. A particular advantage of th compound is that it does not possess any persistent activity and thus it can be successfully employed in crop rotations (Proc. N. Cent. Weed Control Conf. 26, 64 /1971/).

N-phosphonomethyl-glycine is most often prepared by oxydation of N-phosphonomethyl iminodiacetic acid. One known process comprises oxydating the starting material by hydrogen peroxide (Dutch Laid Open Patent Publication No. 73 07 449). According to another method the acetic acid group of the starting material is split off by acid catalysed hydrolysis (Hungarian

Patent Specificati n No. 165 965). El ctrolytic oxydati n is disclosed in German Federal Republic Patent Specification No. 2 363 634 US Patent Specification No. 3 859 183, and British Patent Specification No. 1 452 644. In reference No. 1 N-phosphonomethyl imino diacetic acid is subjected to anodic oxydation in acidic medium by using graphite electrodes, whereas the last two references relate to oxydation carried out on the tetraester group of N-phosphonomethyl imino diacetic acid and the aimed end product is for ed by hydrolysing the obtained N-phosphonomethyl glycine triester.

Oxydation of N-phosphonomethyl imino diacetic acid may also be carried out with oxygen or oxygen-containing gas in the presence of a catalyst (US Patent Specification No. 3 969 398, German Federal Republic Patent Specification No. 2 519 388 and Belgian Patent Specification No. 851 995). The advantage of the catalytical oxydation over the known methods mentioned above is that it does not require expensive chemicals or electrolysing equipments. Severe drawbacks of this method, however come from the fact that N-phosphomethyl-imino diacetic acid used as starting material is poorly soluble in water (saturation concentration of the compound at 25°C: 1 % by weight, at 95°C: 4 % by weight and even at 150°C i.e. even in cases when operations are conducted at a higher pressure than normal pressure, the solubility amounts only to 10 % by weight (see German Federal Republic Patent Specification No. 2 519 388).

As a consequence of the minimal solubility of N-phosphonomethyl imino diacetic acid aqueous solutions have to be employed in a large amount reducing thereby the useful capacity of the reactor and increasing thus the required energy. A large amount of water has to be removed from the effluents requiring a further amount of energy. This process is thus uneconomical considering both utilization of capacity and energy balance.

In order to eliminate the disadvantages mentioned above a method is disclosed in Belgian Patent Specification No. 851 995, according to which the salts of N-phosphonomethyl-imino diacetic acid are used as starting material. Depending upon the character of the cation being present, the salts of N-phosphonomethyl imino diacetic acid form a 5-30 % saturated solution with water of a temperature of 100 °C. From the point of view of energy-saving only those salts may be used in large scale practice, the solubility of which is close to the upper limit of the saturated concentration. Thus for example isopropyl amine salt of N-phosphonomethyl imino diacetic acid may be employed. Data disclosed in Belgian Patent Specification No. 851 995 show that during oxydation of the compound a considerable amount of by-products is formed (such as N-methyl-N-phosphonomethyl glycine and methylamine methyl phosphonic acid), which reduces the yield of the end-product and may be removed from the end-product only with difficulties. Though the formation of by-products may be reduced if conventionally

wood charcoal catalysts are replaced by platinum catalyst (in this case the rat f the main reacti n is selectively increased) side reactions however can never be eliminated completely. A further disadvantage is the low yield of the reaction: isopropylamine salt of N-phosphonomethyl glycine is obtained even in the most favourable case in the form of about 20 % aqueous solution, thus still a large amount of water has to be removed from the solution (about 50 %) if the product is formulated in the commercially available form of a 36 % aqueous solution. This process is however somewhat more economical than the previous process, but neither the purity of the product nor the energy balance of the process are satisfying.

According to the invention the disadvantages of the mentioned known processes are eliminated by preparing pure N-phosphonomethyl glycine by an economic, energy-saving and capacity-increasing process.

We have now found that catalytic oxydation of N-phosphonomethyl imino diacetic acid may be carried out in suspensions converting thus N-phosphonomethyl imino diacetic acid completely to N-phosphonomethyl glycine with a great specific conversion (related to time unit and identical liquid volume).

The process according to the invention was not obvious in the light of the disclosure of German Federal Republic Patent Specification No.2519 388. On the contrary in the cited reference a process is disclosed

comprising the oxydation of N-phosphonomethyl imino diacetic acid carried out in aqueous solutions and not even the use of supersaturated solutions is suggested because: "the precipitation of the starting material can be expected whereby the reaction is slowing down and the separation and purification of the product becomes more difficult."

Similar conclusions could be drawn when considering the reaction mechanics of suspensions. As the reaction may take place only on the boundary surfaces, it can be expected that the reaction - if it takes place at all - will be extremely slow from the beginning, the rate of reaction will gradually decrease with accumulating end-product and when achieving a given concentration the reaction substantially comes to an end as the molecules of the end-product formed on the boundary surface can diffuse only very slowly into the inner part of the liquid layer. Thus even in the most favourable cases only very slow reactions could be expected in suspensions, where 100 % conversion is not achieved. We have now surprisingly found that the amount of the starting material converted within one time unit (expressed in grams) in a suspension is about twice as much as the amount obtained in the reaction conducted in liquid layer and at the same time the starting material can be completely converted to the end-product. It has to be noted that none of the conventionally used methods is used in order to accelerate the reaction in suspensions

(such as pregrinding in a colloid mill, treatment with wetting agents etc.).

The invention relates to an improvement in the process for the preparation of N-phosphonomethyl glycine by oxydating N-phosphonomethyl imino diacetic acid with oxygen or oxygen-containing gas in the presence of a catalyst. The process is characterized by conducting the oxydation of N-phosphonomethyl imino diacetic acid in an aqueous suspension.

The content of N-phosphonomethyl-imino diacetic acid of the aqueous suspension may vary within a relatively wide range. The lower limit is given by the solubility of N-phosphonomethyl imino diacetic acid at a given temperature, while the upper limit depends on the miscibility of the reaction mixture. If the reaction is carried out at 100 °C, then 5 % suspensions may be used as a lower limit but obviously suspensions containing 30-40-50 % of solid may preferably be used.

Oxydation is carried out with oxygen or a gas mixture containing oxygen, such as air. If as oxydating agent pure oxygen is employed, the rate of reaction is higher than the rate of oxydation conducted with air, but considering the needed equipments, energy and labour when pure oxygen is prepared, it is more economic to use air as oxydating agent.

The reaction temperature may vary within relatively wide limits. The reaction is carried out at a temperature ranging from room temperature to 200 °C, preferably from

50 to 150 °C, mor pref rably fr m 70 to 120 °C.

The reaction may be conducted at normal pressure but the reaction rate is rather low when working under normal pressure. The reaction is preferably carried out at elevated pressure, such as 2-20 atm. It is particularly preferred if the reaction is conducted at 4-10 atm. Further improvement is not achieved, when increasing pressure above this value.

Oxydation is always conducted under shaking or stirring. The rate of shaking or stirring should be sufficient to give a homogeneous suspension, local inhomogeneities may slow down the reaction and thus the end products may contain impurities.

As catalysts known catalysts, such as powder formed or granular charcoal (e.g. German Federal Republic Patent Specification No. 2 519 388), noble metal catalysts on a carrier (e.g. platinum or palladium applied on active charcoal), noble metaloxyde catalysts (such as platinum oxyde) and so on may be employed. Noble metal catalysts applied on active coal (preferably platinum and palladium catalyst) ensure a higher initial rate of reaction than the active coal catalysts, i.e. they act as rate increasing catalysts as disclosed in Belgian Patent Specification No. 861 996 . Active charcoal may be separated by simple filtration and it may be fully recovered by washing with hot water and by drying at 100-120 °C. The separated catalyst may be suspended in hot water followed by a treatment with an

oxygen-c ntaining gas, e.g. with air and followed by drying. The catalytic activity of the recov red cataly t has not decreased after 10 working cycles.

According to Belgian Patent Specification No. 651 955 active charcoal used as a catalyst of the oxydation carried out in a solution looses its activity after a few cycles and cannot be recovered anymore.

According to the invention, however no significant losses in the material were observed in the course of the recovery of the catalyst.

At least 5 mg. of catalyst are used per 1 g. starting N-phosphonomethyl imino diacetic acid. The upper limit of the amount of the catalyst is substantially giv n by economic viewpoints. The amount of the catalyst may be e.g. 0.5-100 %, preferably 5-60 %, particularly 5-40 % of the amount of N-phosphonomethyl imino diacetic acid.

According to the process of the invention N-phosphonomethyl glycine is obtained in the form of a pure product shown by NMR spectroscopy. The obtained aqueous solution may be concentrated, if desired, according to the demands of the user, or N-phosphonomethyl glycine may be separated in solid form as well. Solutions obtained according to the invention and containing N-phosphonomethyl glycine may after distilling off formaldehyde, directly be employed for agrochemical purposes.

The further Examples serve merely as illustration and not for limitation.

Example 1

Comparative Example

The reaction is carried out in an acid-fast 200 ml. cylindrical steel tank equipped with a heating jacket, thermometer, and an air-introducing and air-outlet valve. To the reactor a solution of 4 g. of N-phosphonomethyl iminodiacetic acid in 100 ml. of water of a temperature of 100 °C is added and to the solution 0.4 g. of Norit A catalyst is introduced. The reactor is sealed, fixed on a shaker and to the reactor air is introduced until a pressure of 6 atm. is achieved. The reaction is carried out at 90-95 °C under steady stirring of the reactor. The formaldehyde and carbon dioxide formed during the reaction is blown out from the reactor every 30 minutes. Under such conditions the reaction is completed within 2.5 hours and thus 2.8 g. (100 %) of pure N-phosphonomethyl glycine are obtained (purity verified by NMR spectroscopy). Specific conversion is calculated according to the following formula:

$$\text{specific conversion} = \frac{\text{weight of end product (g.)}}{\underset{\text{(liter)}}{\text{volume of liquid}} \times \underset{\text{(hour)}}{\text{reaction time}}}$$

Specific conversion: 11.2 g./l.hour

Example 2

One may proceed according to Example 1 but as starting material 100 g. of water, 20 g. of N-phosphonomethyl imino diacetic acid and as catalyst 2 g. of Norit

A are used. After a reaction time of 6.5 hours 14 g. of N-phosphonomethyl glycine are obtained and thus the specific conversion amounts to 21.5 g./liters.hour. (1.9 times more than the value achieved according to the comparative Example).

Example 3

One may proceed as disclosed in Example 1 but as starting material 100 g. of water, 40 g. of N-phosphonomethyl imino diacetic acid and as catalyst 4 g. of Norit A catalyst are used. After a reaction time of 10 hours 28.6 g. of pure N-phosphonomethyl glycine are obtained (verified by NMR spectroscopy). Specific conversion: 28.6 g./liters.hour (2.5 times more than the value obtained in the comparative Example).

Example 4

One may proceed as disclosed in Example 1 but as starting material 100 g. of water, 30 g. of N-phosphonomethyl imino diacetic acid and as catalyst 3 g. of Norit A catalyst are employed. After a reaction time of 8.5 hours 21.2 g. of pure N-phosphonomethyl glycine are obtained (verified by NMR spectroscopy). Specific conversion: 24.9 g./liters.hour (2.2 times more than the value achieved by the comparative Example).

Example 5

The reaction is carried out in a 2 liters acid-

fast and pr ssure resisting steel autoclave equipp d with a heating jacket, thermometer, air introducing and air outlet valve and paddle stirrer. To the autoclave 300 g. of N-phosphonomethyl imino diacetic acid, 1000 ml. of water and 30 g. of Norit A are introduced. The autoclave is sealed, the reaction mixture is heated to 90-95 °C, and air is led to the autoclave under the liquid level until 6 atm pressure is achieved. The suspension is stirred at a rate of 400 rpm. After a reaction time of 8.5 hours 208 g. of pure N-phosphonomethyl glycine are obtained, the purity of which is checked by NMR spectroscopy. Achieved specific conversion: 24.4 g./liters.hour (2.2 times more than the value obtained by the comparative Example).

When the reaction is completed, the catalyst is immediately filtered off, the mixture is washed with hot water and dried at 110 °C. The thus recovered catalyst is used in further operations.

Example 6

One may proceed as disclosed in Example 5, but as starting material 1000 ml. of water, 200 g. of N-phosphonomethyl imino diacetic acid and as catalyst 20 g. of Norit A recovered as disclosed in Example 5 are used. After a reaction time of 6.5 hours, 146 g. of N-phosphonomethyl glycine, the purity of which is verified by NMR spectroscopy, are obtained. Achieved specific conversion: 22.4 g./liters.hour (twice the value obtained

in the comparative Example).

The catalyst is recov red as described in Exampl 5 and used in further operations.

Example 7

One may proceed as described in Example 1 but as starting material 100 ml. of water, 20 g. of N-phosphonomethyl imino diacetic acid and as catalyst 2 g. of Norit A catalyst-recovered again after the reaction disclosed in Example 6 - a-- used. After a reaction time of 6.5 hours 14.2 g. of pure N-phosphonomethyl-glycine are obtained, the purity of which is verified by NMR spectroscopy. Achieved specific conversion: 21.8 g./liters.hour (1.9 times more than the value achieved according to the comparative Example).

The catalyst is used in further five working cycles after recovery. The activity of the catalyst is not reduced.

Example 8

One may proceed as disclosed in Example 1 but as starting material 100 ml. of water, 20 g. of N-phosphonomethyl imino diacetic acid and as catalyst 5 % palladium/charcoal (Carbo C Extra) are employed. After a reaction time of 5 hours 14.4 g. of pure 4-phosphonomethyl glycine are obtained, the purity of which is verified by NMR spectroscopy. Achieved specific conversion: 28.8 g./liters.hour (2.5 times more than the

value obtained in the comparative Exampl).

Example 9

One may proceed as disclosed in Example 1 but as starting material 100 ml. of water, 20 g. of N-phosphonomethyl imino diacetic acid and as catalyst 2 g. of Carbo C Extra are employed. After 7 hours reaction time 14.3 g. of pure N-phosphonomethyl glycine are obtained the purity of which was checked by NMR spectroscopy. Achieved specific conversion: 20.8 g./liters.hours (1.85 times more than the value achieved by the comparative Example).

Example 10

One may proceed as disclosed in Example 1 but as starting material 100 ml. of water, 20 g. of N-phosphonomethyl imino diacetic acid and as catalyst 2 g. of 5 % platinum/charcoal (Carbo C Extra) are used. After a reaction time of 4.5 hours 14.2 g. of pure N-phosphonomethyl glycine are obtained the purity of which is checked by NMR spectroscopy. The achieved specific conversion: 31.5 g./liters.hours (2.8 times more than the value obtained by the comparative Example).

When comparing data of Examples 8 to 10, it can be observed that by using noble metals the reaction rate may be increased.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

~~Claims~~

1. Process for the preparation of N-phosphonomethyl-glycine by oxydating N-phosphonomethyl imino diacetic acid with oxygen or a gas containing oxygen under shaking or stirring in the presence of a catalyst (conventional) at a temperature of between room temperature and 200°C which comprises oxydating N-phosphonomethyl imino diacetic acid in an aqueous suspension therefore.

2. A process as claimed in claim 1 comprising using a suspension containing 7-70 g. of N-phosphonomethyl imino diacetic acid related to 100 ml. water as starting material.

3. A process as claimed in claim 2 which comprises using a suspension containing 20 to 50 g. of N-phosphonomethyl imino diacetic acid related to 100 ml. of water as starting material.

4. A process as claimed in any of the claims 1 to 3 which comprises using air as a gas containing oxygen.

5. A process as claimed in any of the previous claims, which comprises conducting the reaction at elevated pressure.

6. A process as claimed in any of the previous claims which comprises using active charcoal as catalyst, separated after the reaction by filtration and recovered by washing with hot water, and drying at 100 to 120 °C.

7. A process as claimed in claim 6 which comprises washing the catalyst with hot water during the introduction of oxygen or a gas containing oxygen,

preferably air below the liquid level.

DATED this 8th day of May 1980.

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